Fig. 1.

70; RbF, 36; RbCl, 54; RbBr, 62; RbI, 76; Cs 85; CsF, 45; CsCl, 60; CsBr, 68; CsI, 81 cc./ mole.

The values of $A_{12}$ for the sodium systems from $T_c$ are, respectively, 215, 155, 136, 120 cal./cc., which are considerably larger than those in Table II for the heavier metals. We note that the value of $A_{12}$ from $T_c$ is the lowest for each potassium system and corresponds, of course, to the highest temperature. Presumably this is the result of a large excess partial molal entropy, as was found for the the sodium systems, and which yields a negative temperature coefficient for $\Delta\mu^0$. Where values based upon both $\gamma_{metal}$ and $\gamma_{salt}$ are available in Table II, they are nearly equal, which indicates conformity to the volume fraction equations. This is further indicated in Fig. 1 which shows the data for RbBr in a manner to test equation 2.

## Discussion

The preceding calculations and arguments have shown that the valence electrons from the alkali metal atoms in a metal–fused salt solution may be considered to be a negative ion species much like the halide ions themselves. The general similarity of the solubility properties of these systems to the corresponding properties of mixtures of non-polar molecules has been noted as well as the significant differences. It is clear that the mixing of the two negative species must be nearly random. However, if the metal concentration is high, we know that the valence electrons assume metallic character and that it is no longer a useful approximation to regard a particular electron localized in a particular cavity. One must now regard the array of cavities as an irregular lattice of sites of low potential energy for electrons and solve the many-electron problem for electronic motion in and among these sites. The work of Lax and Phillips[13] shows that the irregular geometry itself does not qualitatively change the electronic energy level pattern. The decisive matters with respect to metallic vs. non-metallic character are those discussed by Mott.[14] The overlap of the wave functions between the F-center cavities is a critical factor. As Mott predicts, intermediate states are unstable at low temperatures, and one finds the continuous transition from metallic to non-metallic character only above a critical mixing temperature.

The metal to non-metal transition composition may be taken to be that of the critical point for phase separation. It is interesting to note that this composition is of the order of 50 mole % metal for the fused salt solutions whereas it is only 4.2% metal in solutions of sodium in liquid ammonia. Apparently the electronic wave functions are much more localized in the fused salts than in ammonia.

Additional properties such as electrical conductance[15] can be shown to be consistent with our general model. We may also note that the system[16] Li–LiH appears to be similar to the halide systems.

(13) M. Lax and J. C. Phillips, Phys. Rev., 110, 41 (1958).
(14) N. F. Mott, Phil. Mag., [8] 6, 287 (1961); N. F. Mott and W. D. Twose, Adv. in Phys., 10, 107 (1961); and earlier papers there cited.
(15) H. R. Bronstein, A. S. Dworkin and M. A. Bredig, J. Chem. Phys., 34, 1843 (1961); also J. Am. Chem. Soc., 80, 2077 (1958).
(16) C. E. Meiser, et al., J. Phys. Chem., 62, 220 (1958).

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# Association Constants in the System $AgNO_3$–$NaBr$–$NaNO_3$ and their Comparison with the Quasi-lattice Theory

BY D. L. MANNING,[1] R. C. BANSAL,[2] J. BRAUNSTEIN[3] AND M. BLANDER

The association constants $K_1$, $K_2$ and $K_{12}$ for the formation of AgBr, $AgBr_2^-$ and $Ag_2Br^+$ have been evaluated from electromotive force measurements in $AgNO_3$–$NaBr$–$NaNO_3$ mixtures at 402, 438, 460 and 500°. The constants, $K_1$, $K_2$ and $K_{12}$, in mole fraction units, are, respectively, 633, 246 and 280 at 402°, 500, 180 and 200 at 438°, 430, 151 and 167 at 460° and 325, 103 and 120 at 500°. The temperature dependence of the association constants, within the experimental error, is predictable from calculations based on the quasi-lattice model. The differences between values of $K_1$ for the formation of AgBr in $NaNO_3$ and $KNO_3$ are consistent with the "reciprocal coulomb effect."

## Introduction

Measurements of the activity coefficients of $AgNO_3$ in molten $NaNO_3$ in dilute solutions of $Ag^+$

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and $Br^-$ ions at four temperatures ranging from 402 to 500° are described in this paper. One of the

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(4) Operated for the United States Atomic Energy Commission by Union Carbide Corporation.

purposes of these measurements was to further[5] demonstrate that the temperature coefficients of the association constants, $K_1$, $K_2$ and $K_{12}$ for the formation of the groupings Ag–Br, $AgBr_2^-$ and $Ag_2Br^+$ respectively, are, within the experimental precision, correctly predicted by the expressions derived from calculations based on the quasi-lattice model[6]

$$K_1 = Z (\beta_1 - 1) \quad (1)$$

$$K_1 K_2 = Z \left(\frac{Z-1}{2}\right) (\beta_1\beta_2 - 2\beta_1 + 1) \quad (2)$$

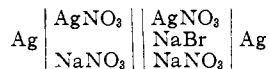$$K_1 K_{12} = Z \left(\frac{Z-1}{2}\right) (\beta_1\beta_{12} - 2\beta_1 + 1) \quad (3)$$

where $\beta_i = \exp(-\Delta A_i/RT)$, $\Delta A_i$ is a "specific bond free energy" and is independent of temperature and $Z$ is a coördination number. The second purpose of the measurements was to obtain information on the solvent effect by comparing these measurements with those made in the $AgNO_3$–$KBr$–$KNO_3$[7] system and also with the corresponding chloride containing systems in molten $NaNO_3$ and $KNO_3$. This comparison appears to provide a clue to the physical parameters which account in a large part for the differences between association constants in the two solvents $NaNO_3$ and $KNO_3$.

## Experimental

Reagent grade NaBr was dried at 400° and stored in a desiccator. Otherwise, the materials, apparatus and procedure were essentially the same as described previously.[5]

## Results

Activity coefficients were calculated from electromotive force measurements in the cell

$$\text{Ag} \left| \begin{matrix} AgNO_3 \\ NaNO_3 \end{matrix} \right| \left| \begin{matrix} AgNO_3 \\ NaBr \\ NaNO_3 \end{matrix} \right| \text{Ag}$$

using the equation

$$\Delta E = \frac{2.303\ RT}{F} \log \gamma_{AgNO_3}$$

where $\Delta E$ is the change of e.m.f. upon the addition of NaBr to the right hand electrode compartment at a fixed concentration of $AgNO_3$ at concentrations of $Ag^+$ and $Br^-$ ions too low to precipitate AgBr. In Table I are given measured values of $\Delta E$ in this system at several concentrations of $AgNO_3$ at 402, 438, 460 and 500°. The solubility of AgBr is smaller in $NaNO_3$ than in $KNO_3$ and hence measurements in $NaNO_3$ were made over a smaller range of concentrations than in $KNO_3$.

**Evaluation of the Association Constants $K_1$, $K_{12}$ and $K_2$.**—The association constants $K_1$, $K_{12}$ and $K_2$ which correspond to the groupings AgBr, $Ag_2Br^+$ and $AgBr_2^-$ were evaluated using a method previously described.[8] Large scale plots of $-\log \gamma_{AgNO_3}$ (or of $-\Delta E$) were made as a function of the mole ratio of NaBr ($R_{NaBr}$) at several fixed concentrations of $AgNO_3$ ($R_{AgNO_3}$) (mole ratios are the

ratio of the moles of component indicated to moles of solvent). The limiting slopes of these plots were obtained graphically at $R_{NaBr} = 0$ and were plotted as a function of $R_{AgNO_3}$ at 402, 438, 460 and 500°. The plots were linear with a small negative slope. At 402°, because of the low solubility of AgBr, there was appreciable scatter in such a plot. From the equations for mass balance and for concentrations low enough so that all solute ions and associated species obey Henry's law, it can be shown that the equation $-2.303 \log \gamma_{AgNO_3} = K_1 R_{NaBr} + (K_1 K_2 - \frac{1}{2}K_1^2)R^2_{NaBr} + (2K_1K_{12} - K_1^2)R_{NaBr} R_{AgNO_3} + ..$ holds. From the comparison of this equation with a MacLaurin series expansion of $\log \gamma_{AgNO_3}$ in terms of the variables $R_{NaBr}$ and $R_{AgNO_3}$, it can be shown[8] that the intercepts of the plots of the slopes which are

$$\lim_{\substack{R_{NaBr}=0 \\ R_{AgNO_3}=0}} \left(\frac{\partial \log \gamma_{AgNO_3}}{\partial R_{NaBr}}\right) \text{ are equal to } (-K_1/2.303)$$

and the limiting slopes which are

$$\lim_{\substack{R_{NaBr}=0 \\ R_{AgNO_3}=0}} \left(\frac{\partial^2 \log \gamma_{AgNO_3}}{\partial R_{NaBr}\partial R_{AgNO_3}}\right) \text{ are equal to}$$

$$[(K_1^2 - 2K_1K_{12})/2.303]^8$$

Values of $K_1$ and $K_{12}$ evaluated in this manner from the intercepts and the slopes are given in Table II. Values of $K_2$ were evaluated by a least squares fit of $-\log \gamma_{AgNO_3}$ at fixed concentrations of $AgNO_3$ to the equation

$$-\log \gamma_{AgNO_3} = A R_{NaBr} + B R_{NaBr}^2$$

A plot of $-B$ versus $R_{AgNO_3}$ was relatively linear. The extrapolated limit of $-B$, designated $-B_0$, at $R_{AgNO_3} = 0$ which is

$$\frac{1}{2}\lim_{\substack{R_{NaBr}=0 \\ R_{AgNO_3}=0}} \left(\frac{\partial^2 \log \gamma_{AgNO_3}}{\partial R_{NaBr}^2}\right)$$

is equal to $\left(\frac{\frac{1}{2}K_1^2 - K_1K_2}{2.303}\right)$ and was used to evaluate the values of $K_2$ given in Table II. A relatively large error in $B_0$ leads to a relatively small error in $K_2$.

## Discussion

The derived values of $K_1$, $K_2$ and $K_{12}$ given in Table II were used to calculate values of the "specific bond free energies," $\Delta A_i$, from equations 1–3. Values of $\Delta A_1$, $\Delta A_2$ and $\Delta A_{12}$ calculated in this way are given in Table II and within the estimated experimental precision of the measurements are constant over the entire range of temperatures studied and for $Z = 4$, 5 and 6 which should cover all reasonable values of this parameter. This indicates that equations 1–3 lead to a prediction of the temperature coefficients of $K_1$, $K_2$ and $K_{12}$ which are correct within the estimated experimental precision of the measurements. The constancy of the calculated values of $\Delta A_i$[9] appears to be insensitive to the choice of reasonable values of $Z$.

A comparison of the values of $\Delta A_1$ for the associations of $Ag^+$ and $Cl^-$ and of $Ag^+$ and $Br^-$ in the two molten solvents $NaNO_3$ and $KNO_3$ is made in

(5) (a) M. Blander, F. F. Blankenship and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959). (b) J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960). (c) D. G. Hill, J. Braunstein and M. Blander, *ibid.*, **64**, 1038 (1960). (d) D. G. Hill and M. Blander, *ibid.*, **65**, 1866 (1961).

(6) (a) M. Blander, *ibid.*, **63**, 1262 (1959). (b) M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960). (c) M. Blander *J. Chem. Phys.*, **34**, 342 (1961).

(7) A. Alvarez-Funes, J. Braunstein and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962).

(8) J. Braunstein, M. Blander and R. M. Lindgren, *ibid.*, **84**, 1529 (1962).

(9) Where the change in the internal degrees of freedom of the ions involved in the association process is small, the relations $\frac{d\Delta A_i}{dT} \cong 0$ and $\Delta A_i \cong \Delta E_i$ should be valid.

## TABLE I

### E.M.F. CHANGES OF THE CELL AT DIFFERENT TEMPERATURES UPON THE ADDITION OF SODIUM BROMIDE

#### Temperature 402°

| $R_{AgNO_3} = 0.050 \times 10^{-3}$ | | $R_{AgNO_3} = 0.061 \times 10^{-3}$ | | $R_{AgNO_3} = 0.078 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.141 | 6.14 | 0.0543 | 1.15 | 0.103 | 4.50 |
| .350 | 14.00 | .179 | 6.25 | .262 | 10.33 |
| .568 | 19.68 | .285 | 9.95 | .420 | 16.30 |
| .934 | 30.24 | .437 | 15.20 | .627 | 23.82 |
| 1.28 | 38.80 | .636 | 22.56 | 1.02 | 34.42 |
| 1.67 | 48.50 | .855 | 29.95 | 1.26 | 41.60 |
| 2.18 | 58.00 | 1.19 | 40.03 | 1.60 | 51.35 |
| 2.65 | 70.50 | 1.58 | 48.66 | 2.15 | 65.17 |
| 3.20 | 82.60 | 2.04 | 59.70 | 2.59 | 74.44 |
| 3.81 | 94.00 | 2.51 | 71.68 | 3.00 | 83.20 |
| 4.70 | 110.80 | 3.02 | 82.63 | 3.62 | 96.10 |
| | | 3.82 | 97.38 | 4.32 | 108.95 |
| | | 4.76 | 113.37 | 4.60 | 113.00 |

| $R_{AgNO_3} = 0.108 \times 10^{-3}$ | | $R_{AgNO_3} = 0.169 \times 10^{-3}$ | | $R_{AgNO_3} = 0.225 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.093 | 4.08 | 0.105 | 3.90 | 0.070 | 2.55 |
| .167 | 7.26 | .255 | 9.60 | .158 | 6.25 |
| .285 | 11.25 | .413 | 15.60 | .306 | 11.37 |
| .467 | 17.87 | .584 | 21.25 | .389 | 14.76 |
| .685 | 24.40 | .770 | 27.90 | .520 | 19.55 |
| .830 | 30.36 | 1.02 | 37.10 | .616 | 24.45 |
| 1.00 | 35.50 | 1.30 | 50.30 | | |
| 1.23 | 42.26 | | | | |
| 1.61 | 54.36 | | | | |
| 2.00 | 65.80 | | | | |
| 2.44 | 77.18 | | | | |
| 3.13 | 92.60 | | | | |

#### Temperature 402°

| $R_{AgNO_3} = 0.249 \times 10^{-3}$ | | $R_{AgNO_3} = 0.271 \times 10^{-3}$ | | $R_{AgNO_3} = 0.400 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.139 | 5.65 | 0.059 | 2.10 | 0.124 | 4.00 |
| .358 | 13.36 | .134 | 5.10 | .214 | 7.15 |
| .583 | 23.90 | .205 | 7.70 | .328 | 11.43 |
| | | .274 | 10.32 | | |
| | | .352 | 14.43 | | |
| | | .426 | 17.20 | | |
| | | .494 | 20.10 | | |

#### Temperature 438°

| $R_{AgNO_3} = 0.0530 \times 10^{-3}$ | | $R_{AgNO_3} = 0.106 \times 10^{-3}$ | | $R_{AgNO_3} = 0.204 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.047 | 1.80 | 0.067 | 2.80 | 0.141 | 3.66 |
| .138 | 3.95 | .175 | 5.85 | .261 | 6.96 |
| .254 | 6.65 | .296 | 9.40 | .427 | 13.26 |
| .327 | 8.25 | .419 | 13.46 | .611 | 18.17 |
| .425 | 10.15 | .730 | 21.25 | .778 | 22.46 |
| .530 | 12.65 | .975 | 29.03 | 1.01 | 27.35 |
| .738 | 16.50 | 1.38 | 42.30 | 1.28 | 34.35 |
| .862 | 19.33 | 1.93 | 51.10 | 1.64 | 44.87 |
| 1.065 | 23.26 | 2.48 | 60.85 | 2.00 | 54.05 |
| 1.231 | 26.30 | 3.18 | 71.20 | 2.49 | 64.10 |
| 1.46 | 29.80 | 3.82 | 81.45 | 2.98 | 73.26 |
| 1.66 | 34.48 | 4.44 | 90.00 | | |
| | | 4.72 | 103.90 | | |

#### Temperature 438°

| $R_{AgNO_3} = 0.265 \times 10^{-3}$ | | $R_{AgNO_3} = 0.345 \times 10^{-3}$ | | $R_{AgNO_3} = 0.440 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.108 | 2.93 | 0.209 | 5.35 | 0.069 | 0.85 |
| .196 | 5.60 | .389 | 10.80 | .147 | 3.55 |
| .367 | 13.45 | .660 | 19.30 | .264 | 6.93 |
| .646 | 19.66 | .934 | 28.05 | .386 | 9.90 |
| .762 | 23.02 | 1.25 | 40.35 | .523 | 14.60 |
| .982 | 29.94 | | | .684 | 19.77 |
| 1.19 | 34.52 | | | .817 | 24.07 |
| 1.38 | 39.90 | | | | |
| 1.54 | 44.77 | | | | |
| 1.84 | 52.70 | | | | |

#### Temperature 460°

| $R_{AgNO_3} = 0.126 \times 10^{-3}$ | | $R_{AgNO_3} = 0.192 \times 10^{-3}$ | | $R_{AgNO_3} = 0.212 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.279 | 7.9 | 0.266 | 7.3 | 0.167 | 4.5 |
| .574 | 14.7 | .576 | 15.8 | .395 | 11.5 |
| .890 | 22.3 | .890 | 22.5 | .615 | 17.5 |
| 1.18 | 28.9 | 1.22 | 31.7 | 1.02 | 26.6 |
| 1.56 | 35.6 | 1.59 | 39.8 | 1.41 | 37.0 |
| 2.01 | 42.4 | 2.11 | 49.7 | 1.89 | 47.0 |
| 2.53 | 52.4 | 2.59 | 59.7 | 2.38 | 55.4 |
| 3.12 | 59.3 | 3.24 | 70.3 | 2.87 | 63.5 |
| 3.52 | 65.0 | 3.86 | 79.6 | 3.32 | 70.4 |
| 4.02 | 72.0 | 4.24 | 84.5 | 3.77 | 78.1 |
| 4.32 | 76.8 | 4.62 | 89.9 | 4.36 | 86.4 |
| 4.72 | 82.1 | 4.85 | 92.8 | 4.80 | 92.5 |

#### Temperature 460°

| $R_{AgNO_3} = 0.328 \times 10^{-3}$ | | $R_{AgNO_3} = 0.472 \times 10^{-3}$ | | $R_{AgNO_3} = 0.621 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.303 | 8.1 | 0.0954 | 2.60 | 0.0952 | 2.1 |
| .564 | 15.4 | .241 | 6.50 | .1537 | 3.5 |
| .855 | 22.5 | .400 | 10.60 | .2683 | 6.5 |
| 1.18 | 30.4 | .581 | 14.80 | .3969 | 10.3 |
| 1.57 | 38.9 | .804 | 20.70 | .7242 | 19.4 |
| 1.98 | 48.0 | .958 | 24.20 | | |
| 2.39 | 56.5 | 1.16 | 29.50 | | |
| 2.84 | 65.7 | 1.38 | 36.10 | | |
| 3.35 | 75.6 | | | | |
| 3.92 | 85.9 | | | | |
| 4.54 | 95.3 | | | | |
| 4.95 | 101.2 | | | | |

#### Temperature 500°

| $R_{AgNO_3} = 0.130 \times 10^{-3}$ | | $R_{AgNO_3} = 0.226 \times 10^{-3}$ | | $R_{AgNO_3} = 0.308 \times 10^{-3}$ | |
|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.250 | 5.5 | 0.193 | 4.50 | 0.236 | 4.8 |
| .490 | 10.2 | .504 | 10.90 | .555 | 11.3 |
| .845 | 17.0 | .793 | 17.45 | .861 | 17.6 |
| 1.14 | 22.5 | 1.22 | 25.50 | 1.21 | 24.5 |
| 1.71 | 31.1 | 1.62 | 33.70 | 1.61 | 32.1 |
| 2.16 | 38.0 | 2.21 | 43.05 | 2.20 | 42.6 |
| 2.77 | 47.0 | 2.71 | 51.54 | 2.79 | 52.3 |
| 3.58 | 57.1 | 3.38 | 61.40 | 3.44 | 61.7 |
| 4.11 | 62.8 | 3.89 | 68.46 | 4.08 | 70.2 |
| 4.63 | 68.7 | 4.23 | 72.65 | 4.42 | 75.1 |
| 4.96 | 71.4 | 4.51 | 77.14 | 4.73 | 78.7 |
| | | 4.74 | 79.75 | | |

#### Temperature 500°

| $R_{AgNO_3} = 0.298 \times 10^{-3}$ | | $R_{AgNO_3} = 0.564 \times 10^{-3}$ | | $R_{AgNO_3} = 1.00 \times 10^{-3}$ | | $R_{AgNO_3} = 2.02 \times 10^{-3}$ | |
|---|---|---|---|---|---|---|---|
| $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. | $R_{NaBr} \times 10^3$ | $\Delta E$, mv. |
| 0.1218 | 2.4 | 0.0930 | 1.8 | 0.1452 | 3.1 | 0.0785 | 1.4 |
| .3442 | 7.4 | .2227 | 4.8 | .3132 | 6.5 | .1640 | 2.6 |
| .5572 | 11.8 | .4791 | 10.0 | .4940 | 10.0 | .2481 | 4.2 |
| .7258 | 15.2 | .6718 | 14.3 | .6402 | 13.0 | .3234 | 5.7 |
| 1.031 | 21.6 | .7270 | 15.5 | .8768 | 17.7 | .4484 | 8.0 |
| 1.094 | 23.6 | .9122 | 19.3 | 1.094 | 22.0 | .5795 | 10.5 |
| 1.358 | 28.8 | 1.131 | 23.7 | | | | |
| 1.468 | 30.3 | 1.425 | 30.0 | | | | |

Table III. The values of $\Delta A_1$ for an arbitrarily-chosen value of $Z = 5$ was used for this comparison, although the comparison of $\Delta A_1$ calculated using any other reasonable choice of $Z$ would lead to the same conclusions. In column 4 are given the values of $[\Delta A_1(NaNO_3) - \Delta A_1(KNO_3)]$ for the formation of AgCl or AgBr. Since $K_1 = Z[\exp(-\Delta A_1/RT) - 1]$, then for values of $\exp(-\Delta A_1/RT)$ large relative to unity

$$[\Delta A_1(NaNO_3) - \Delta A_1(KNO_3)] \cong RT \ln \frac{K_1(KNO_3)}{K_1(NaNO_3)}$$

The differences in $\Delta A_1$ from $NaNO_3$ and from $KNO_3$ may be rationalized with the help of Fig. 1, which is a two dimensional representation of the association process and where $A^+ = Ag^+$, $B^+ =$

TABLE II

VALUES OF $K_1$, $K_2$ AND $K_{12}$ AND DERIVED VALUES OF THE "SPECIFIC BOND FREE ENERGY" FOR ASSOCIATIONS OF $Ag^+$ AND $Br^-$ IN NaNO$_3$

| | | $T$ (°K.) | 675° | 711° | 733° | 773° | |
|---|---|---|---|---|---|---|---|
| $K_1$ | (moles/mole NaNO$_3$)$^{-1}$ | | 633 | 500 | 430 | 325 | |
| $K_2$ | (moles/mole NaNO$_3$)$^{-1}$ | | 246 | 180 | 151 | 103 | |
| $K_{12}$ | (moles/mole NaNO$_3$)$^{-1}$ | | (280)$^a$ | 200 | 167 | 120 | |
| $-\Delta A_1$ | (kcal./mole) | | 6.79 | 6.82 | 6.83 | 6.74 | } $Z = 4$ |
| $-\Delta A_2$ | (kcal./mole) | | 6.9 | 6.8 | 6.7 | 6.5 | |
| $-\Delta A_{12}$ | (kcal./mole) | | 7.0 | 6.9 | 6.9 | 6.7 | |
| $-\Delta A_1$ | (kcal./mole) | | 6.51 | 6.52 | 6.50 | 6.43 | } $Z = 5$ |
| $-\Delta A_2$ | (kcal./mole) | | 6.5 | 6.4 | 6.3 | 6.1 | |
| $-\Delta A_{12}$ | (kcal./mole) | | 6.6 | 6.5 | 6.5 | 6.3 | |
| $-\Delta A_1$ | (kcal./mole) | | 6.27 | 6.26 | 6.24 | 6.16 | } $Z = 6$ |
| $-\Delta A_2$ | (kcal./mole) | | 6.2 | 6.1 | 6.0 | 5.8 | |
| $-\Delta A_{12}$ | (kcal./mole) | | 6.3 | 6.2 | 6.1 | 6.0 | |
| Estimated % error in $K_1$ | | | ± 5 | ± 3 | ± 3 | ± 4 | |
| Estimated % error in $K_2$ | | | ±20 | ±10 | ±10 | ±20 | |
| Estimated % error in $K_{12}$ | | | ±25 | ±15 | ±15 | ±20 | |

$^a$ Calculated from scattered data; error about 25%.

TABLE III

COMPARISON OF AVERAGE VALUES OF $\Delta A_1$ FOR THE FORMATION OF AgCl AND AgBr ION PAIRS IN NaNO$_3$ AND KNO$_3$

$$[\Delta A_1 \text{ (NaNO}_3\text{)} - \Delta A_1 \text{ (KNO}_3\text{)}] \cong RT \ln \frac{K_1 \text{ (KNO}_3\text{)}}{K_1 \text{ (NaNO}_3\text{)}}$$

| Ion pair | Solvent | $\Delta A_1$ ($Z = 5$) (kcal./mole) | Measured | Coulombic calculation Nearest neighbor | Infinite chain |
|---|---|---|---|---|---|
| AgCl | NaNO$_3$ | −4.83 | 1.05 | 2.58 | 1.78 |
| | KNO$_3$ | −5.88 | | | |
| AgBr | NaNO$_3$ | −6.50 | 0.64 | 1.41 | 0.97 |
| | KNO$_3$ | −7.14 | | | |

$Na^+$ or $K^+$, $C^- = Cl^-$ or $Br^-$ and $D^- = NO_3^-$. As discussed previously[7] the largest contributions to the absolute values of $\Delta A_1$ for the formation of AgCl and AgBr are probably from the van der Waals energy. Other effects will be superimposed on this effect and may vary with the solvent.

A likely contribution to the solvent effect is from a "reciprocal coulomb effect." In Fig. 1 it can be seen that the major change which takes place upon the formation of an AC ion pair is the interchange of nearest neighbor BC and AD pairs to form AC and BD. If the interionic distance for BD is $r$, for BC is $r(1 + \Delta_1)$ for AD is $r(1 + \Delta_2)$ and for AC is $r(1 + \Delta_1 + \Delta_2)$ then the interchange of ions illustrated in the lower part of Fig. 1 will lead to a change in the coulombic energy unless $\Delta_1$ or $\Delta_2$ or both are zero. If $\Delta_1$ and $\Delta_2$ have the same sign, the energy change is negative and if they are of opposite sign, the energy change is positive.[10] Under the assumption that the effective ionic radii are $Ag^+ = 1.20$, [11]$Na^+ = 0.98$ [12]$K^+ = 1.33$ $NO_3^- = 2.19$; $Cl^- = 1.81$, and $Br^- = 1.95$ Å., the differences in the coulombic energy of nearest neighbors given in Column 5 of Table III were calculated. The relative values of the calculated differences for the chloride and bro-

(10) For discussions of this and related phenomena see E. B. Thomas and L. J. Wood, *J. Am. Chem. Soc.*, **56**, 92 (1934); **57**, 822 (1935). T. Förland, "On the Properties of Some Mixtures of Fused Salts," N. T. H. Trykk, Trondheim, Norway, 1958.

(11) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961), in press. The calculated energy differences in Table III are very insensitive to the choice of the radius of $Ag^+$.

(12) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., 1958, p. 28.

mide containing systems listed in Table III are the same as the observed differences but are larger in magnitude. Although the effect of long range interactions cannot be assessed easily in terms of a
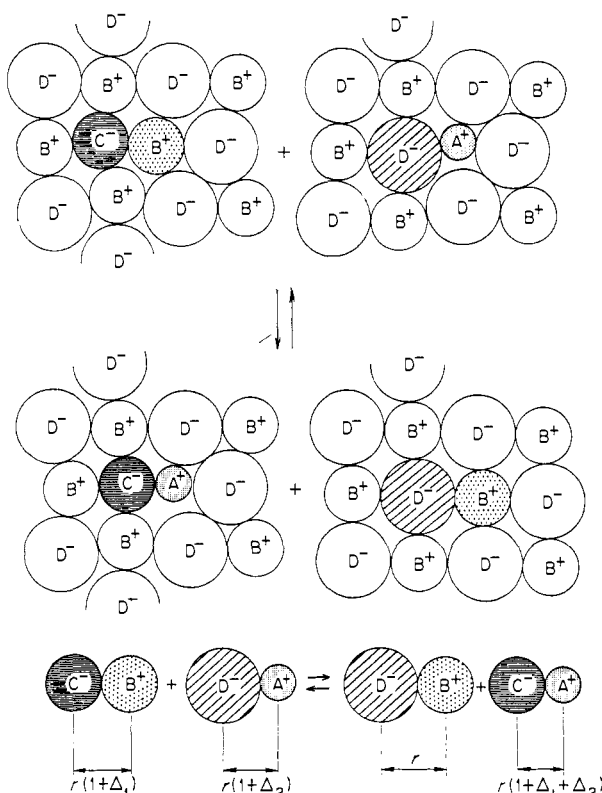


Fig. 1.—Two dimensional representation of the "reciprocal coulomb effect."

realistic three dimensional model, calculations of the "reciprocal coulomb effect" for the infinite one dimensional chains …BDBDBCBDBD…+… BDBDADBDBD…⇌…BDBDACBDBD…+ …BDBDBDBDBD… using a method of calculation similar to one described previously[13] led to the equation for the total change of energy, $\Delta U$

(13) M. Blander, *J. Chem. Phys.*, **34**, 697 (1961).

$$\frac{r\Delta U}{e^2} = \sum_1^\infty (-1)^n \left[ - \left( \frac{1}{n + \Delta_1} \right) - \left( \frac{1}{n + \Delta_2} \right) + \right.$$

$$\left( \frac{1}{n + \Delta_1 + 2\Delta_2} \right) + \left( \frac{1}{n + 2\Delta_1 + \Delta_2} \right) +$$

$$\left( \frac{-2(1 + \Delta_1 + \Delta_2)}{n + 2\Delta_1 + 2\Delta_2} \right) + \left( \frac{1 + 2\Delta_1}{n + 2\Delta_1} \right) + \left. \left( \frac{1 + 2\Delta_2}{n + 2\Delta_2} \right) \right] +$$

$$\frac{1}{1 + \Delta_1 + 2\Delta_2} + \frac{1}{1 + 2\Delta_1 + \Delta_2} - \frac{1}{1 + \Delta_1 + \Delta_2} -$$

$$\frac{1}{1 + 2\Delta_1 + 2\Delta_2} \quad (4)$$

Calculated values of $\Delta U(\text{NaNO}_3) - \Delta U(\text{KNO}_3)$ are listed in Column 6 of Table III and are about 0.7 times the value based on the nearest neighbor calculation. Although these calculations cannot be correct for a real three dimensional system, they serve to assess the importance of long range coulombic interactions. Other effects, as for example a polarization effect, would probably lead to a larger solvent effect for the bromide containing systems. Since the calculated coulombic effect is in the same direction as the observed differences, it is likely that at least part of the effect is coulombic. It is important to note that the relative sizes of both cations *and* both anions enter into this effect. If the solvent anion $D^-$ were smaller than the solute anion $C^-$ and all others ions were the sizes used in the calculation, then the sign of the energy of the "*reciprocal coulombic effect*" would be changed.

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# A Thermodynamic and Kinetic Study of Hexachloro and Aquopentachloro Complexes of Iridium(III) in Aqueous Solutions[1]
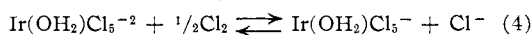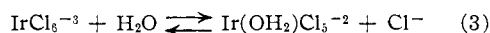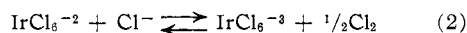
BY INGEBORG A. POULSEN AND CLIFFORD S. GARNER

A spectrophotometric study of the kinetics of aquation of $IrCl_6^{-3}$ and of $Cl^-$ anation of $Ir(OH_2)Cl_5^{-2}$ in 1.0–2.5 $F$ $HClO_4$ (or HCl) at 50° has led to evaluation of rate constants and the equilibrium constant $K$ for the reversible reaction $IrCl_6^{-3} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ir(OH_2)Cl_5^{-2} + Cl^-$. Aquation of $IrCl_6^{-3}$ was studied at 6–50° in 1.0–2.5 $F$ $HClO_4$ by a spectrophotometric method and in 1.0 $F$ $HClO_4$ by a titrimetric method. At 25.05° and $\mu = 2.2$, $k_1 = (9.4 \pm 0.6) \times 10^{-6}$ sec.$^{-1}$, $E_a = 30.4 \pm 2.0$ kcal., and log $PZ = 17.5 \pm 1.8$. At 50.05° $k_1$ is independent of $(IrCl_6^{-3})_0$ over the range 0.5–11.5 m$F$ ($\mu = 2.2$), of $(Cl^-)_0$ over the ranges 0–2.2 $M$ ($\mu = 2.2$) and 1.0–3.4 $M$ ($\mu = 3.4$), and, in $HClO_4$, of $(H^+)$ between 1.0–2.5 $M$ ($\mu = 3.6$–3.7); $k_1$ decreases as $\mu$ increases from 2.2–3.4. At 1 $M$ $H^+$ and 50.05° the anation rate law was found experimentally to be $-d(Ir(OH_2)Cl_5^{-2})/dt = k_{-1}(Ir(OH_2)Cl_5^{-2})(Cl^-)$, with $k_{-1} = 5 \times 10^{-6}$ $M^{-1}$ sec.$^{-1}$, approximately independent of $\mu$ between 2.2 and 3.4; $k_{-1}$ increases with $(H^+)$ in the range 1.0–2.5 $M$ ($\mu = 3.4$–3.7). $K$ varies between 2.2 and 9.3 $M$ at 50° in these solutions. The first-order rate constant for aquation of $Ir(OH_2)Cl_5^{-2}$ is $\leq 0.1k_1$ at 25 and 50°. A simple new method was developed for the preparation of $Na_3IrCl_6 \cdot 2H_2O$.

During continued studies[2-4] of hexachloro complexes of iridium(III) and iridium(IV) in this Laboratory a need arose to investigate the aquation of hexachloroiridate(III) anion. The inability of the reversible reactions

$$IrCl_6^{-2} + H_2O \rightleftharpoons Ir(OH_2)Cl_5^- + Cl^- \quad (1)$$
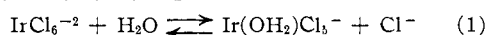
to account fully for the observed decrease in rate of chloride ion release during aquation of hexachloroiridate(IV) anion at 50°,[4] together with experiments made by us at 115° with $IrCl_6^{-2}$ in hydrochloric acid solutions either saturated with $Cl_2$ or $Cl_2$-free, indicate that reactions 1 in $Cl_2$-free solutions may in some way be linked to oxidation–reduction reactions, possibly through the reaction sequence

$$IrCl_6^{-2} + Cl^- \rightleftharpoons IrCl_6^{-3} + \frac{1}{2}Cl_2 \quad (2)$$

$$IrCl_6^{-3} + H_2O \rightleftharpoons Ir(OH_2)Cl_5^{-2} + Cl^- \quad (3)$$

$$Ir(OH_2)Cl_5^{-2} + \frac{1}{2}Cl_2 \rightleftharpoons Ir(OH_2)Cl_5^- + Cl^- \quad (4)$$

Reversible interconversion of $IrCl_6^{-3}$ and $Ir(OH_2)Cl_5^{-2}$ *via* reaction 3 has long been known.[5,6] More recently conductometric[7,8] and spectrophotometric[9] methods were employed to study qualitatively the aquation of $IrCl_6^{-3}$ in aqueous solutions; in the conductometric work acid was not present and the results may have been influenced by base hydrolysis. Except for several isotopic exchange studies and kinetic investigations of the base hydrolysis of hexachloroantimonate(V) anion[10] and aquation of hexachlororuthenate(III) anion,[11] no quantitative kinetic studies appear to have been published on metal hexahalo complexes in aqueous solution.

In the present work we have followed reaction 3 from both sides partly spectrophotometrically

(1) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University.

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